

THE EISENHOWER LIBRARY



3 1151 02678 0183

98.094

Library



Johns Hopkins University
of the



A FURTHER INVESTIGATION
OF THE ACTION OF
PHENOLS AND ALCOHOLS ON THE CHLORIDES
OF
PARANITROORTHOSULPHOBENZOIC ACID.

--oo--

A Dissertation presented to the Board of
University Studies of the Johns Hopkins Uni-
versity for the Degree of Doctor of Philoso-
phy.

By

Victor John Chambers.

1901.

Johns Hopkins University,
Baltimore, Maryland.

98097

Contents.

	Page
Acknowledgement.-----	4
Introduction.-----	5
Preparation of Materials. -----	7
PART I. Action of Phenols upon the Symmetrical and Unsymmetrical Chlorides of Paranitroorthosul- phobenzoic Acid. -----	11
1. Phenol, -----	13
2. Orthocresol.-----	18
3. Paracresol. -----	20
4. Orthonitrophenol.-----	23
5. Paranitrophenol,-----	25
6. Metanitrophenol,-----	26
7. Resorcinol, -----	26
8. Hydroquinone, -----	28
9. Betanaphthol,-----	29
10. Paraamidophenol, -----	31
11. Action of various reagents upon the parani- troorthosulphonchloride of pheryl benzoate, 32	
12. Action of various reagents upon the diphe- nyl ester of paranitroorthosulphoben- zoic Acid. -----	45

PART II.	Action of Alcohols upon the Unsymmetrical	
	Chloride of Paranitroorthosulphobenzoic Acid,	47
1.	Methyl Alcohol, -----	49
2.	Ethyl Alcohol, -----	51
3.	Propyl Alcohol.-----	53
 PART III.	 The Action of Phenol in Ammonia Solution	
	upon the two Chlorides of Paranitroortho-	
	sulphobenzoic Acid. -----	57
 Conclusions,	-----	61
Biographical.	-----	64.

Acknowledgement.

The investigation herein described was undertaken at the suggestion of Professor Remsen and the work was done under his supervision. I desire, in this place, to express my profound gratitude to him for the help and inspiration he has been to me both in the laboratory and in the lecture room.

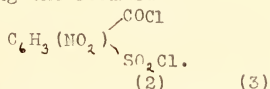
I wish also to express my thanks to Professor Morse, Dr. H. C. Jones and Dr. D. S. Johnson for instruction received from them.

A FURTHER INVESTIGATION OF THE ACTION OF PHENOLS AND ALCOHOLS ON THE CHLORIDES OF PARANITROORTHOSULPHOBENZOIC ACID.

Introduction.

-oo-

The first work on the product of the reaction between the acid potassium salt of paranitroorthosulphobenzoic acid (1) and phosphorus pentachloride was that of Kastle. This product was a wax-like solid that dissolved readily in chloroform and ether crystallizing therefrom in yellow needles or plates having a melting-point of 60°. He considered it a substance having the formula



The work of Remsen and Coates, Remsen and Kohler, and Remsen and McKee showed that the corresponding reaction product obtained from the acid potassium salt of orthosulphobenzoic acid was not a single substance, but a mixture of two isomeric substances.

-
- (1) Am. Chem. Jour., 11., 177.
 (2) Ibid. 17, 311.
 (3) Ibid. 17, 330.
 (4) Ibid. 18, 794.

(1)

Gray isolated the two corresponding chlorides of paranitroorthosulphobenzoic acid and studied the action of ammonia and of aniline upon them.

(2)

The next year Hollis studied the action of benzene in the presence of aluminium chloride upon the chlorides (3) and the properties of the resulting compound. Henderson later continued the investigation of the two isomeric chlorides (4) and finally Holmes studied the action of urea upon the same substances.

From this work, and particularly from the action of ammonia and of aniline on these chlorides, the higher melting one was called the symmetrical chloride and given the

formula $\text{C}_6\text{H}_3(\text{NO}_2) \begin{cases} \text{COCl} \\ \text{SO}_2\text{Cl} \end{cases}$; the other was named the unsym-

metrical with the formula $\text{C}_6\text{H}_3(\text{NO}_2) \begin{cases} \text{C} \begin{cases} \text{Cl}_2 \\ \text{O} \end{cases} \\ \text{SO}_2 \end{cases}$

This investigation is divided into three parts, (1) the action of phenols upon the symmetrical and the unsymmetrical chlorides of paranitroorthosulphobenzoic acid, (2) the action of alcohols upon the unsymmetrical chloride, and the (3)

(1) Ibid. 19, 496.

(2) Ibid. 23, 233.

(3) Ibid. 25, 1.

(4) Ibid. 25, 202.

action of a mixture of phenol and ammonia upon both the chlorides of this acid. The review of the work previously done on each of these topics is given as an introduction to each part.

PREPARATION OF MATERIAL.

Paranitrotoluene was used as the starting-point. From this the acid and the neutral potassium salt of paranitroorthosulphobenzoic acid were obtained and from these, in turn, the symmetrical and unsymmetrical chlorides of the same acid.

Acid Potassium salt of Paranitroorthosulphobenzoic (1)

Acid.- It was made by the method worked out by Hart, Kas-
(2) (3) (4) (5)
tle, Gray, Hollis, and Henderson. The method will be described in full as the author found some details convenient in obtaining a good and pure yield. 300 grams of powdered paranitrotoluene were added to 1200 grams of fuming sulphuric acid contained in a large balloon flask. The flask and its contents were placed in a water-bath and heated until the fumes of sulphur trioxide began to come off in quanti-

-
- (1) Am. Chem. Jour. 1, 340.
 - (2) Loc. cit.
 - (3) Loc. cit.
 - (4) Loc. cit.
 - (5) Loc. cit.

ty. The mixture was kept warm and thoroughly stirred until a small portion, added to cold water, dissolved to a clear solution. About two hours of such treatment was generally sufficient.

When the reaction was complete, the mixture was poured into ~~three 6 0 saxon~~ dishes previously filled with water. It was then neutralized with calcium carbonate, filtered first through muslin, then paper and the gypsum thoroughly washed. The filtrate, which contains the calcium salt of paranitroorthosulphotoluene, was heated to boiling and treated with a solution of potassium carbonate so long as precipitation occurred. It was then filtered and the filtrate evaporated until a small portion, when cooled, deposited crystals of the potassium salt of paranitroorthosulphotoluene.

Fifty grams of this salt were added to about three litres of water contained in a five-litre balloon flask. This was then heated in a water-bath and steam passed into it. When the salt was dissolved and the contents had begun to boil, there was added 15 grams of potassium hydroxide dissolved in a little water. 110 grams of powdered potassium permanganate were then added in small portions and the solution boiled until the color of the permanganate had dis-

appeared.

This generally occurs after about six hours boiling if the process has been continuous. Henderson draws attention to the fact that both the potassium ^{salt-} of paranitroorthosulphotoluene and the potassium hydroxide must be in solution before they are brought together; otherwise a red coloring matter is formed.

The author further found that a yellow to a yellowish red was developed if the oxidation was stopped for over night or longer. The best results were obtained by the continuous process described above. When the color of the permanganate had disappeared, the solution was filtered hot and the oxides of manganese washed thoroughly with hot water. The filtrate and washings were neutralized with hydrochloric acid and evaporated to a small volume. Concentrated hydrochloric acid was then added and the acid potassium salt of paranitroorthosulphobenzoic acid separated in fine silky crystals on cooling.

THE NEUTRAL POTASSIUM SALT OF PARANITROORTHOSULPHOBENZOIC ACID. - ^{Th.} It was formed by dissolving the acid salt in water and adding potassium hydroxide to neutral reaction. The solution was then evaporated to dryness and the residue

very finely powdered.

THE SYMMETRICAL CHLORIDE. - The process described by Henderson (1) was used. It was found best to allow the dry chloroform solution to evaporate at the room temperature. If an attempt be made to concentrate this solution by distilling off the excess of chloroform, slight decomposition occurs and it is very difficult to get a pure product from the residue.

THE UNSYMMETRICAL CHLORIDE. - It was prepared as described by Holmes (2). The method in detail is as follows: The neutral potassium salt of paranitroorthosulphobenzoic acid, finely powdered, was heated in a sealed tube with 1 1/2 molecules of phosphorus oxychloride for four hours at 135°. The product was transferred to a good sized mortar and ground up with ice water. It was found impossible to filter off the solid material at first, but the crude chloride became granular by standing for an hour to an hour and a half in ice water.

The chloride could then be readily collected on a muslin filter and washed thoroughly with ice water. After it had become completely dry, it crystallized from pure ligroin. Care should be taken to keep the ligroin below the

(1) Loc. cit.

(2) Loc. cit.

melting-point of the chloride.

PART I. - THE ACTION OF PHENOLS UPON THE SYMMETRICAL AND
 UNSYMMETRICAL CHLORIDES OF PARANITROORTHOSUL-
 PHOBENZOIC ACID.

The action of phenol upon the chlorides of orthosul-
 phobenzoic acid has been studied. Remsen and Saunders
 (1)
 used the mixed chlorides and the symmetrical chloride. Rem-
 sen and McKee, (2) both the symmetrical and the unsymmetrical
 chlorides.

In every case a diphenyl ester and a red coloring
 matter supposed to be a sulphophthalein were obtained.
 (3)
 Humphreys repeated the work of Remsen and McKee and showed
 that, besides the two substances referred to, a third sub-
 stance was obtained if the temperature was kept down.

This proved to be the orthosulphon-chloride of phen-
 yl benzoate.

Less work has been on the action of phenols upon the
 chlorides of paranitroorthosulphobenzoic acid. Henderson
 (4)

-
- (1) Loc cit.
 (2) Loc cit.
 (3) Loc cit.
 (4) Loc cit.

tried the action of various phenols on the symmetrical chloride and ~~had~~ obtained, with phenol and ortho- and para-cresols, results analogous to those of Remsen and McKee.

It was thought best, therefore, to make a comparative study of the action of phenols upon the symmetrical chloride with that upon the unsymmetrical chloride.

The method in general ~~use~~ was to mix a few grams of the chloride with slightly more than the required amount of the phenol and to heat this mixture in a test tube immersed in a bath of sulphuric acid. A large amount of the phthalein is formed in this way which makes the product very difficult of purification. Humphreys showed that the Schotten-Baumann reaction could be applied to this case. He heated a mixture of the chloride and the phenol in a beaker until it liquified.

A cold dilute solution of potassium hydroxide was then added and the oily mass stirred occasionally until it solidified. After washing and crystallization from glacial acetic acid a very clean pure product was obtained.

Both these methods were used by the author. In some cases where they did not give good results a third, or rather, a modification of the second method was used. This consisted in adding an alcoholic potassium hydroxide solution

to an alcoholic solution of the chloride and phenol mixture. Potassium chloride separated and the reaction-product was obtained from the solution either by adding water slowly or by evaporation ^{of} the alcohol. In some cases, where the reaction-product was but slightly soluble in alcohol, it separated with the potassium chloride. After thorough washing with water, it was crystallized from glacial acetic acid.

I. ACTION OF PHENOL UPON THE TWO CHLORIDES OF PARANITRO-ORTHOSULPHOBENZOIC ACID. -

a. Upon the Symmetrical Chloride:- Three grams of the symmetrical chloride were mixed with slightly more than the calculated amount of phenol and heated in a test tube in the acid bath to 135°.

The results obtained were similar to those described by Henderson. The product was the diphenyl ester melting (1) at 118° - 119°. Humphreys had obtained both the diphenyl ester and a small amount of the orthosulphonchloride of phenyl benzoate by a similar treatment of the symmetrical chloride of orthosulphobenzoic acid. The reaction mixture in this case was examined for the corresponding orthosul-

(1) Loc. cit.

phosphonchloride, but none was discovered.

A small portion of symmetrical chloride was mixed with an excess of phenol and heated in a beaker until they melted. ^A Dilute solution of potassium hydroxide was then added and the oily mass stirred until it solidified and crumbled.

The time required varied with the strength of the alkaline solution and the temperature. If that solution is moderately strong and the mixture heated on a water-bath the action is over in five minutes.

The crumbly mass was filtered off, washed, and crystallized from glacial acetic acid or alcohol.

Beautiful needles of the diphenyl ester were obtained, melting-point 118° .

A small portion of the symmetrical chloride and the necessary amount of phenol were dissolved in alcohol. To this solution was added an alcoholic solution of potassium hydroxide, until precipitation of potassium chloride had ceased. Impure diphenyl ester was obtained from the solution. After recrystallization from glacial acetic acid it melted at 118° .

b. Upon the Unsymmetrical Chloride:- Three grams of the unsymmetrical chloride were mixed with a slight excess

of phenol in a test tube which was placed in a sulphuric acid bath. Heat was applied and the temperature raised slowly to 135° where it was kept for four hours. As soon as the substances melted a red color was developed which increased in depth until it became almost black. Hydrochloric acid commenced to come off at almost 100° . ^{the evolution} It increased in rapidity as the temperature rose, decreasing again after heating a short time at 135° . The black mass became somewhat viscous but did not harden on cooling. The cooled mass was treated with water which dissolved much of the coloring matter and caused the mass to harden.

The red solution so obtained was turned to a deep purple on the addition of an alkali. After as much of the coloring matter had been extracted in this ^{way} _^ as was possible, the crumbly mass was decanted upon a filter and washed first with dilute alkali, then with hot water. The residue was recrystallized several times from glacial acetic acid. Light brown heavy needles were obtained which melted poorly at 145° - 147° . These proved to be the para-nitroorthosulphonch chloride of phenyl benzoate.

The question came up whether any di ϕ phenyl ester
(1)
was formed by this process. Humphreys, working with the

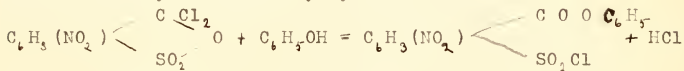
(1) Loc. cit.

unsymmetrical chloride of orthosulphobenzoic acid, had obtained both products, the amount of each depending on the temperature used. He found that, working at the lowest temperature at which the reaction would occur, he got a mixture containing, besides the phenyl ester chloride, a little of the diphenyl ester, while, if the temperature was raised, more diphenyl ester was found until at a temperature just below the decomposition point practically ^{only} ~~all~~ diphenyl ester was ^{formed} ~~had~~. This change is easily understood when we take into consideration the fact, that he showed in another experiment, that his phenyl ester chloride reacts itself with phenol at a high temperature forming diphenyl ester. No diphenyl ester was found in the product of the reaction between phenol and the unsymmetrical chloride of paraniroorthosulphobenzoic acid. It will be shown later that the paranitro^oorthosulphonch chloride of phenyl benzoate, or, as it is often called, phenyl ester chloride, does not react with phenol even when heated to the highest temperature short of decomposition.

A few grams of the unsymmetrical chloride were melted with an excess of phenol. The beaker was placed on ice and to the oily mass was added a cold dilute solution of potassium hydroxide. The mass solidified very slowly. Af-

ter washing and crystallization from glacial acetic acid pure crystals of phenyl ester chloride were obtained which melted at 146° . It is necessary to keep the temperature of the reaction low and the alkaline solution weak, for if not some or all diphenyl ester is obtained.

Paranitroorthosulphonchloride of phenyl benzoate was made for analysis and study by this method:



Analysis of the substance gave the following results:

0.2662 gram gave 0.4465 gram CO_2 and 0.0660 gram H_2O

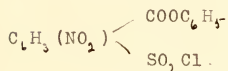
0.3147 gram gave 0.1308 gram AgCl

0.2746 gram gave 0.1108 gram AgCl

0.3560 gram gave 0.0146 gram nitrogen.

Calculated for

Found.



C	45.68	45.76
H	2.74	2.34
Cl	10.37	10.28
N	4.10	4.10



II. ACTION OF ORTHOCRESOL UPON THE TWO CHLORIDES OF
PARANITROORTHOSULPHOBENZOIC ACID.

a. Upon the Symmetrical Chloride. - The results obtained by the heating together of these two substances were in
(1)
perfect accord with those obtained by Henderson.

A few grams of the symmetrical chloride were heated with the same weight of orthocresol in a test tube in an acid bath. A slight red color developed as soon as they melted and grew darker as the temperature rose. Hydrochloric acid commenced to come off at about 110° . The temperature was raised to 135° for three hours when a black mass was obtained that grew hard on cooling. Washing with warm dilute solution of sodium hydroxide left a very little black residue which gave but a trace of a dark crystalline material on crystallizing from glacial acetic acid.

Equal parts of the chloride and orthocresol were melted together. Dilute solution of potassium hydroxide was added and the mass stirred occasionally. The oily mass did not solidify perfectly even after two days standing. It was dissolved in glacial acetic acid from which

(1) Loc. cit.

solution rosettes of small crystals were obtained melting at $95^{\circ} - 97^{\circ}$.

They were probably impure crystals of the unchanged chloride.

An alcoholic solution of potassium hydroxide was added slowly to an alcoholic solution of equal parts of the chloride and orthocresol. Granular crystals of potassium chloride at once separated. On allowing the alcoholic solution to evaporate a crystalline mass was obtained that gave, upon recrystallization from glacial acetic acid, heavy needles melting at 90° .

This substance must be the same as was obtained in small quantity by Henderson by the fusion method. No analysis was made by him or the author, but there is little doubt that it was the diorthocresylester of paranitroorthosulphobenzoic acid.

b. With the Unsymmetrical Chloride - The phenomena observed when these two substances were heated together were about the same as when the symmetrical chloride was used. Evolution of hydrochloric acid began a few degrees lower and the product did not become so hard on cooling. A much larger residue was left after washing ^{and then when} which, upon crystal-

^{adv}
~~lization~~ from glacial acetic acid gave small dark plates melting poorly at 148° .

The Schotten-Baumann method gave better results. The mass hardened slowly and gave pure white plates melting at 150° when crystallized from glacial acetic acid. These proved to be the paranitroorthosulphonchloride of orthocresyl benzoate.

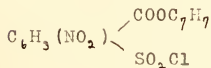
Analysis:

0.3237 gram gave 0.5647 gram CO_2 and 0.0916 gram H_2O .

0.3456 gram gave 0.1365 gram Ag Cl.

Calculated for

Found.



C	47.26	47.57
H	2.81	3.29
Cl	9.96	9.74

III. ACTION OF PARACRESOL UPON THE TWO CHLORIDES OF PARANITROORTHOSULPHOBENZOIC ACID.

a. Upon the Symmetrical Chloride. - Equal parts of the symmetrical chloride and paracresol were melted together in a sulphuric acid bath. A red color was developed quickly

and deepened as the temperature rose. Hydrochloric acid was observable at 100° . The temperature was raised to 115° and kept there for four hours, after which the ^{mass} ~~melt~~ was treated with cold water. It soon hardened and after washing as before and recrystallization ^{ing} from glacial acetic acid short, thick needles were obtained which melted rather badly at 116° .

Equal parts of the symmetrical chloride and paracresol were melted together and treated with a five per cent, solution of potassium hydroxide.

The mass became oily, but hardened after two days. After washing and crystallization from glacial acetic acid fine heavy needles were obtained melting at 118° . The substance was the diparacresylester of paranitroorthosulpho-
(1)
benzoic acid ~~and~~ obtained by Henderson by the first of the two above processes.

b). Upon the Unsymmetrical Chloride. - The reaction was carried on in the same way as with the symmetrical chloride. There was but little difference in the course of the experiment except the end product ^{product} ~~which~~ in this case was the paranitrosulphonchloride of paracresyl benzoate. Hydro-

chloric acid was given off about 100° , and the mass turned from reddish-brown to black. The resultant mass on washing and crystallizing gave small needles or prisms melting at 152° (uncor.). The yield by this reaction is poor and hard to purify, yet it proved to be the only method by which it could be prepared.

The Schotten-Baumann method did not work smoothly in this case, the product being in every case the diparacresylester of paranitroorthosulphobenzoic acid. The reaction could not be made to stop half-way as it did with phenol and orthocresol.

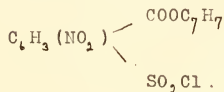
The result of the fusion method proved to be the paranitroorthosulphonchloride of paracresyl benzoate. .

Analysis.

0.2235 gram gave 0.3921 gram CO_2 and 0.0696 H_2O .

0.2571 gram gave 0.1005 gram Ag Cl

Calculated for



Found .

C	47.26	47.87
H	2.81	3.45
Cl	9.96	9.71

IV. - ACTION OF ORTHONITROPHENOL UPON THE TWO CHLORIDES
OF PARANITROORTHOSULPHOBENZOIC ACID.

a. Upon the Symmetrical Chloride. - When heated together in the acid bath action took place slowly. Hydrochloric acid came off somewhat at 100° and was still present after heating to 135° for six hours. The reaction mixture was somewhat colored and still an oil that hardened only slightly on cooling. It was then treated with caustic potash solution which caused hardening in about two days.

Crystallization from glacial acid gave rosettes of needle-shaped crystals melting between 145° and 160° . Equal parts of the phenol and the chloride were melted together and heated with a dilute solution of potassium hydroxide. The oil so formed solidified after five hours' standing to a crumbly mass that on washing and crystallization from glacial acetic acid gave fine needles melting sharply at 164° . This substance proved to be the dinitrophenylester of paranitroorthosulphobenzoic acid as the following analysis shows:

0.1665 gram gave 0.2822 gram CO_2 and 0.0428 gram H_2O .

0.3058 gram gave 0.0261 gram N.

Calculated for		
$C_6H_3(NO_2)$	$COOC_6H_4NO_2$	Found
	$SO_2OC_6H_4NO_2$	
C	46.62	46.25
H	2.05	2.81
N	8.59	8.52

b. Upon the Unsymmetrical Chloride. - Equal parts of the chloride and the phenol were heated in the acid bath as usual. The evolution of hydrochloric acid began about 100° and ^{the mass} ~~it~~ also began to darken. The evolution of hydrochloric acid was slow for, even after heating to 125° for five hours, there was still some acid coming off. The fusion mass had colored brown and was still an oil that hardened but slightly on cooling. ^{A solution of} ~~Caustic soda solution~~ turned it to a crumbly mass after about two days' standing. The mass was washed and crystallized as usual. The product was an impure dinitrophenylester. The Schotten-Baumann method worked very smoothly, the result being rosettes of fine needles that melted sharply at 164°. The action here was evidently to go entirely over to the diorthonitrophenylester. All attempts to get the orthosulphonchloride by modifying the conditions of the experiment were ~~useless~~.

fruit

V. ACTION OF PARANITROPHENOL UPON THE TWO CHLORIDES
OF PARANITROORTHOSULPHOBENZOIC ACID.

a. Upon the Symmetrical Chloride. - The reaction in this case was more vigorous than that between the orthonitrophenol and the chloride. After heating together in an acid bath for five hours at 125° a hard black mass was obtained that dissolved in caustic soda ~~solution~~, but was reprecipitated by acids as a flocculent chocolate colored mass.

It was not further investigated. No ethereal salt was obtained.

The Schotten-Baumann method worked smoothly giving rosettes of thick needles melting at 152° .

The modified Schotten-Baumann method also gave a good yield and a very pure product.

0.1514 gram gave 0.2606 gram CO_2 and 0.0447 gram H_2O

Calculated for

	$\text{C}_6\text{H}_3(\text{NO}_2)\begin{cases} \text{COOC}_6\text{H}_4\text{NO}_2 \\ \text{SO}_2\text{OC}_6\text{H}_4\text{NO}_2 \end{cases}$	Found.
C	46.62	46.93
H	2.05	-----

b. Upon the Unsymmetrical Chloride. - The only difference noticeable between the action of the unsymmetrical chloride and that of the symmetrical was that the unsymmetrical acted a little more readily when fused with the nitrophenol in the acid bath.

VI. - ACTION OF METANITROPHENOL UPON THE SYMMETRICAL CHLORINE OF PARANITROORTHOSULPHOBENZOIC ACID.

The only experiment tried with the metanitrophenol was the action of alcoholic potash upon a similar solution of the chloride and phenol, the modified Schotten-Baumann method. The result was perfectly analogous with those obtained with the other nitro phenols. Small plates melting at 168° uncor. were obtained which, from method of preparation, were probably dimetanitrophenylester of paranitroorthosulphobenzoic acid.

VII. ACTION OF RESORCINOL UPON THE TWO CHLORIDES OF PARANITROORTHOSULPHOBENZOIC ACID.

a. Upon the Symmetrical Chloride. - The reaction of the chloride with resorcinol was the same as described fully by Henderson. The action commenced about 100° and was

~~and was~~ complete after four hours' heating to 130° - 135° . The reaction mass became hard but dissolved readily in sodium hydroxide, a chocolate colored mass being reprecipitated on acidifying.

The Schotten-Baumann method failed in this case; the action being to dissolve out the resorcinol leaving the chloride unacted upon.

When, however, the modified method was used a reaction did occur. The addition of alcoholic potassium hydroxide solution to a similar solution of resorcinol and chloride gave a flocculent precipitate at once. When the alkaline solution was added a red color was developed at first but disappeared on stirring if the alkaline solution were not in excess.

As soon as the color persisted, even after vigorously stirring, the precipitate was filtered off, washed thoroughly with water and alcohol and dried.

The resulting nearly colorless powder was practically insoluble in water, alcohol, glacial acetic acid, ether, chloroform, acetone, or ligroin. The very little that did dissolve in some of these solvents came out again in an amorphous condition. It was readily soluble in caustic alkalies being reprecipitated on acidifying. In the prep-

aration of the substance, if more alkali is added after the color has developed the precipitate dissolves to a reddish green solution. This substance needs further investigation.

b. Upon the Unsymmetrical Chloride: - The action in this case was in the main the same as with the symmetrical chloride, the only difference being that the action took place a little more readily in this case. The same hard mass was obtained which dissolved in alkaline solution and was reprecipitated by acids.

VIII. - ACTION OF HYDROQUINONE UPON THE TWO CHLORIDES OF PARANITROORTHOSULPHOBENZOIC ACID.

a. Upon the Symmetrical Chloride. - Heating together ^{the} in acid bath gave results quite analogous to those obtained with resorcinol and agreeing with those described by Henderson. Hydrochloric acid commenced to come off at 120° the mass becoming dark colored and thick as the heating was continued. The melt became hard on cooling, dissolved readily in alkalies and was reprecipitated, as usual, on the addition of acid.

The Schotten-Baumann reaction gave no better results

in this case than it did with resorcinol. When the modified reaction was used, reaction took place as with resorcinol. The reaction product had similar properties; in fact what has been said about resorcinol can be repeated about the action of the chloride with hydroquinone.

b. Upon the Unsymmetrical Chloride. - Hydrochloric acid commenced to come off at 120° , the ~~melt~~^{mass} becoming dark ~~in~~^{in color} and viscous. After heating to 140° for four hours a black mass was obtained that hardened on cooling and acted like the ~~reaction mixture~~^{product} obtained ~~with~~^{in the case of} the other chloride.

In another experiment the temperature was kept at 125° for two hours. The ~~melt~~^{mass} darkened and thickened somewhat. When caustic soda ~~solution~~^{a solution of} was added part dissolved to a reddish-brown solution and the rest became oily, hardening only on standing. Nothing could be obtained from this mass but unchanged chloride.

IX. ACTION OF B-NAPHTHOL UPON THE TWO CHLORIDES OF PARANITROORTHOSULPHOBENZOIC ACID.

a. - Upon the Symmetrical Chloride. - The action in this case was negative, ~~as far as obtaining~~^{mostly} ~~anything~~^{No} but a coloring material by the fusion method.

Reaction did not take place until the temperature was above 130° . The only product obtained from the hard black reaction product ^{obtained - This gave} was a purple color with alkalis ^{which} ~~be-~~ ^{became} coming red-yellow ^{when it was acidified} on acidifying.

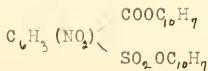
The Schotten-Baumann method gave nothing but unchanged chloride, but when the modified method was used a reaction took place. An alcoholic solution of potassium hydroxide was added to a similar solution of chloride and β -naphthol. A flocculent precipitate at once separated which ^{formed} ~~collected in~~ a gummy mass ^{when stirred} on stirring. The addition of alkali was stopped as soon as the pale brown color produced by it became permanent. The gummy mass became hard on standing. It was then filtered off, washed with water and dilute alkali and crystallized from glacial acetic acid. Beautiful white needles were obtained. Melting-point 134° . Analysis showed it to be the di- β -naphthyl-ester of paranitroorthosulphobenzoic acid.

Analysis.

0.2553 gram gave 0.6017 gram CO_2 and 0.0908 gram H_2O

Calculated for

Found.



C.

64.91

64.30

H.

3.42

3.27

b. Upon the Unsymmetrical Chloride. - There is nothing to add about this reaction ^{to what} ~~than~~ has already been said about that between the naphthol and ^{the} symmetrical chloride when heated in the acid bath. The only method that gave good results with the symmetrical ^{chloride} was, as we have seen, the modified Schotten-Baumann ^{method} and that could not be used with the unsymmetrical chloride because of the reaction that takes place between alcohol and that chloride.

X. ACTION OF PARAAMIDOPHENOL UPON THE UNSYMMETRICAL CHLORIDE OF PARANITROORTHOSULPHOBENZOIC ACID.

Equal parts of the phenol and chloride were heated in the acid bath. No action took place until 125° was reached when a slight evolution of hydrochloric acid was observed. The temperature was kept at 140° for four hours during which time vapors of hydrochloric acid came off slowly and the mass became black and sticky but did not at any time become ^{liquid} ~~a fluid~~. On cooling a hard, shinning, brittle mass was obtained which was insoluble in water but easily so in warm caustic soda ~~solution~~ ^{solution of} to a black solution. On acidifying a chocolate colored precipitate was formed. No ethereal salt was obtained.

The results found in (indicated)

In summing up ^{the} the action of phenols upon the two isomeric chlorides of paranitroorthosulphobenzoic acid, it will be seen that, of the two classes of substances ^{formed} ~~obtained~~, that class in which only one chlorine atom has been replaced by a phenol residue comes only from the unsymmetrical chloride. The other class, that in which both chlorine atoms have been replaced by phenol residues, is the sole product from the symmetrical chloride but may be also made from the unsymmetrical chloride by changing the conditions, providing such change does not destroy the chloride itself.

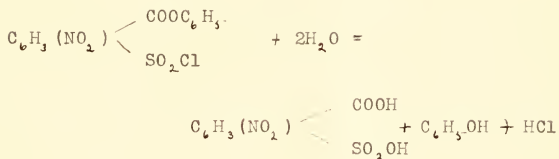
XI. ACTION OF REAGENTS UPON THE PARANITROORTHOSULPHON-CHLORIDE OF PHENYL BENZOATE.

HYDROCHLORIC ACID.

A few grams of the sulphonchloride were boiled with dilute hydrochloric acid in a small flask connected with a return condenser until it had all passed into solution. The saponification took about seven hours. The solution was then carefully evaporated on a waterbath until it just commenced to color. ^{the at} Most of the hydrochloric acid was ^{now} ~~got~~ ten rid of in this way. The syrupy liquid was then diluted

with water, heated to boiling, and neutralized with barium carbonate. As the barium salt formed is sparingly soluble in water, repeated heating with fresh portions of water was necessary to free it from the excess of barium carbonate.

The filtrate was rapidly evaporated over a free flame. The small mica-like plates of the barium salt of paranitroorthosulphobenzoic acid separated during the evaporation.



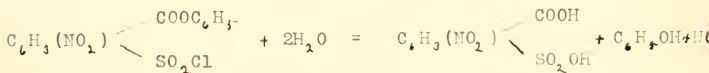
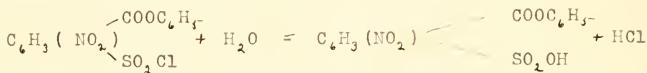
WATER.

A few grams of the sulphonchloride were boiled with water in a flask connected with a return condenser for 10 hours before complete solution took place. The solution was evaporated to a syrup, diluted somewhat and neutralized with barium carbonate. As in the previous experiment, the barium carbonate was repeatedly extracted with boiling water to get out the difficultly soluble barium salt. The solution proved to contain two different barium salts. On

rapid evaporation scale-like crystals resembling in every way the neutral barium salt of paranitroorthosulphobenzoic acid separated while this solution gave on cooling beautiful plates resembling the barium salt of the acid phenyl ester. Owing to lack of material no attempt was made to purify these salts by fractional crystallization; they were simply dried to constant weight and analyzed.

While the results obtained do not correspond well with the calculated percentage of barium, they are what would be expected from these two salts, each contaminated with a small amount of the other.

These results, taken together with the mode of preparation and the physical characteristics leave no doubt that the effect of boiling the sulphonchloride with water is to change part into the acid phenyl ester and part into paranitroorthosulphobenzoic acid:

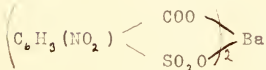


Analyses -

- I. 0.1928 gram of salt that separated from boiling solution gave 0.1150 gram BaSO_4 .
- II. 0.2723 gram of salt that separated on cooling gave 0.0902 gram BaSO_4 .

I. Calculated for

Found.



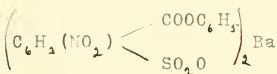
Ba

35.85

35.11

II. Calculated for

Found.



Ba

17.58

19.50

BARIUM HYDROXIDE.

A few grams of the sulphonch chloride were boiled with a clear saturated solution of barium hydroxide for four hours. The liquid never became clear. It was diluted with its own volume of water, heated to boiling and filtered. The insoluble material remaining on the filter was heated to boiling for a few minutes with a little alcohol, then filtered.

On cooling

The filtrate gave ~~on cooling~~ the characteristic crystals of the diphenylester of paranitroorthosulphobenzoic acid; melting-point 118° - 119° . The substance was in all probability the diphenyl ester.

Humphreys obtained the diphenyl ester of orthosulphobenzoic acid by treating the corresponding sulphonchlo-ride in the same way. As he remarks, the formation of this substance here is probably due to a form of the Schotten-Baumann reaction.

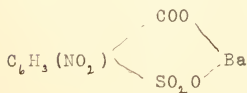
The first filtrate, containing the excess of barium hydroxide and the barium salt of any acid that might have been formed by the reaction, was carefully neutralized with dilute sulphuric acid, heated to boiling and filtered. ^{the filtrate was rapidly evaporated} The filtrate gave ~~on rapid evaporation~~, the characteristic scale like crystals of the neutral barium salt of paranitroorthosulphobenzoic acid.

Analysis of the dried salt:

0.3525 gram gave 0.2149 gram Ba SO₄

Calculated for

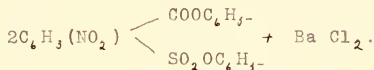
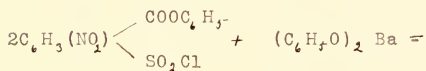
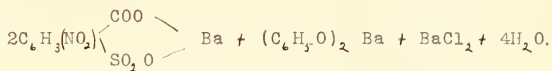
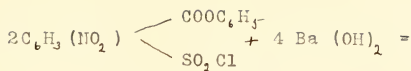
Found.



Ba

35.85

35.88.



ACTION OF AMMONIA.

The action of ammonia was tried under a variety of conditions though with but one result.

It was thought that perhaps the sulphonchloride would give the sulphonamide, but none was obtained. Under all the conditions to be described only nitrobenzoic sulphinid and the diphenyl ester were formed.

A few grams of the phenyl ester chloride were boiled with dilute ammonia in a small flask; fresh portions of am-

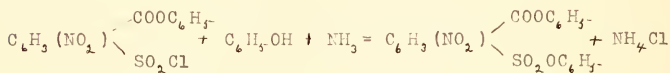
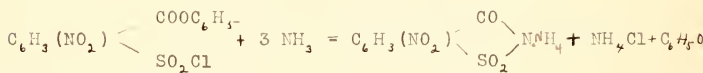
monia solution being added from time to time. The substance did not entirely go into solution even after boiling for twenty hours. The solution was then filtered and the solid residue dissolved in a little alcohol.

Colorless feathery crystals separated on cooling that corresponded well with those of the diphenyl ester and ~~which~~ ^{these} had the correct melting point (119°) for that substance. The aqueous filtrate was evaporated to a small volume, then strongly acidulated with concentrated hydrochloric acid.

Thin plates soon separated that melted at 207° - 208° . When placed upon the tongue they tasted first sweet then very bitter. They were undoubtedly crystals of paranitrobenzoic sulphinide.

A small portion of the sulphonchloride was treated with an excess of concentrated ammonia. No action was apparent until the mixture was heated slightly when the crystalline mass changed its appearance decidedly. The mixture was then filtered, the residue dissolved in a little alcohol from which crystals of diphenyl ester separated on cooling. The filtrate gave nitrobenzoic sulphinide when treated with concentrated hydrochloric acid. Another portion of the sulphonchloride was treated in a dry flask

with dry ammonia. No action took place until the chloride was slightly heated. Fumes of ammonium chloride were then given off and the mass became yellow and soft. ^{Water dissolved} ~~On treatment with water some solution took place.~~ ^{some of the product} The residue proved to be the diphenyl ester. A small amount of the sulphinide was obtained from the solution. Another experiment was tried in which all water was excluded, absolute alcohol being used for the solvent. Diphenyl ester and unchanged chloride were obtained while the alcoholic solution gave a bitter taste upon adding acid. In no case was the sulphonamide obtained. Two reactions appear to take place:

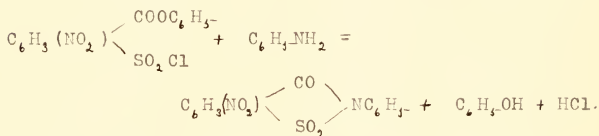


ACTION OF ANILINE.

The action with aniline took place very easily. A few grams of the sulphorchloride were treated with an excess of aniline and heated on the water-bath for a few min-

utes. Solution took place readily. Cold water was added, whereupon an oily mass separated. Dilute hydrochloric acid was added to dissolve the excess of aniline.

The oily mass then soon solidified. This solid dissolved readily in hot alcohol giving, on cooling, fine silky crystals melting at 183° . They were evidently ~~on~~ the (1) anil described by Gray.



ACTION OF ALCOHOLS.

The action of methyl, ethyl, and propyl alcohols was tried with the same result for all.

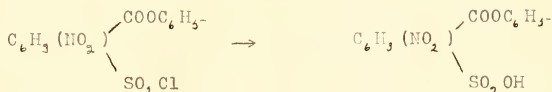
A few grams of the sulphonchloride were treated with absolute alcohol until solution took place. On cooling, crystals of the unchanged sulphonchloride separated. The mixture was then boiled in a small flask connected with a return condenser until the solution no longer became cloudy when diluted with water. This took about five hours.

The solution was then evaporated to a syrup and

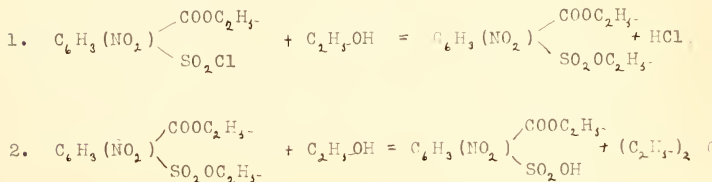
(1) Loc. cit.

heated on a water-bath to get rid of the hydrochloric acid. Care must be taken to stop the heating the moment the least trace of red color appears, otherwise decomposition occurs and phenol is liberated.

Water was added to the syrup and an acid solution obtained from which the following salts were obtained. The reaction with alcohols was merely the passage from paranitroorthosulphonchloride of phenyl benzoate to the corresponding acid phenyl ester:



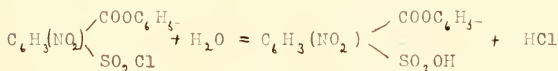
Kastle explains the passage from paranitroorthosulphonchloride of ethyl benzoate to the corresponding acid as first the formation of the diethyl ester and then the reaction of that body with another molecule of alcohol with the formation of the acid ethyl ester and ether.



This explanation will not suffice to show how the

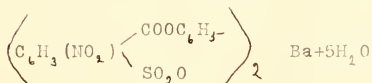
acid phenyl ester is formed as it is shown later that the diphenyl ester can be boiled for hours with alcohol without undergoing change.

As it cannot be truthfully said that so-called "absolute alcohol" is entirely free of water and also that it would take up no water from the air under the conditions of the experiment, it seems simpler to the author to explain this change as the mere passage of a sulphonchloride to its acid by the action of water.



SALTS:-

BARIUM PHENYLPARAMITROORTHOSULPHOPENZOATE,



This salt was made by neutralizing the above acid solution with barium carbonate. It crystallizes from hot water in thin lustrous plates containing five molecules of water of crystallization.

Another salt containing probably six molecules of water of crystallization is formed if the hot solution

cools slowly and quietly. It has the form of close white knobs.

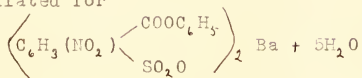
Analysis:

0.2383 gram of the plates lost 0.024 gram H_2O at 170°

0.2134 gram of dried salt gave 0.0635 gram $BaSO_4$.

Calculated for

Found

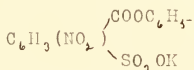


H_2O .	10.34	10.41
----------	-------	-------

Calculated for dry salt

Ba.	17.58	17.51
-----	-------	-------

POTASSIUM PHENYLPARANITROORTHOSULPHOBENZOATE,



This salt was formed by the action of potassium carbonate upon the acid solution. It crystallizes in rather heavy needles with no water of crystallization.

Analysis:

0.2549 gram gave 0.061. gram K_2SO_4 .

Calculated for	$C_6H_3(NO_2) \begin{array}{l} \diagup COOC_6H_5- \\ \diagdown SO_2OK \end{array}$	Found
K.	10.80	10.74

ACTION OF PHENOL.

When the sulphonchloride was heated with phenol in an acid bath a red color was developed after the temperature passed 100° . It was expected that some diphenyl ester would be obtained, but none was found. Even when the temperature was raised to a point short of decomposition the only product that could be gotten out of the melt was unchanged sulphonchloride. The significance of this fact is mentioned in another part of this paper.

While no diphenyl ester was obtained by this method it could be obtained readily from the sulphonchloride by both modifications of the Schotten-Baumann method referred to.

A few grams of the sulphonchloride was melted with phenol and dilute potassium hydroxide ~~solution~~ added. The oily mass soon solidified and diphenyl ester was obtained from the mass by the method already described. When an alcoholic solution of sulphonchloride and phenol is treated with a similar solution of alkali reaction takes place and crystals of diphenyl ester can be obtained by evaporating the solution.

This last method can be used to prepare mixed ethers.

XII. ACTION OF REAGENTS UPON THE DIPHENYLESTER OF PARANITROORTHOSULPHOBENZOIC ACID.

ACTION OF POTASSIUM HYDROXIDE.

A small portion of the diphenyl ester was boiled with a dilute water solution of potassium hydroxide. The ester passed into solution in about five hours.

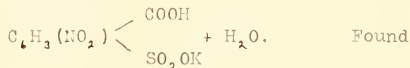
The solution smelled strongly of phenol when acidified and gave a precipitate with bromine water. It was concentrated and treated with concentrated hydrochloric acid. After standing some time feathery crystals resembling the acid potassium salt of paranitroorthosulphobenzoic acid separated.

Analysis: -

0.2959 gram lost 0.0191 gram H_2O below 130°

0.2768 gram gave 0.0865 gram K_2SO_4

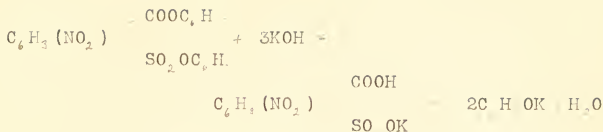
Calculated for



H_2O	5.95	6.45
--------	------	------

Calculated for dry salt

K.	13.69	14.00
----	-------	-------



ACTION OF ALCOHOL.

A few grams of the diphenyl ester were boiled with absolute alcohol for eight hours without change. A little water was added and the boiling was continued for another eight hours. On cooling unchanged diphenyl ester crystallized out. The solution was tested for acid with a negative result.

PART II.

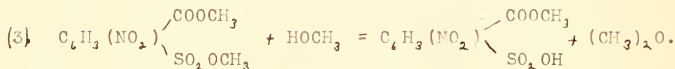
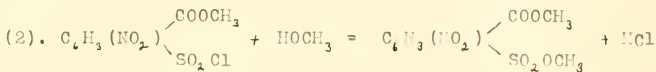
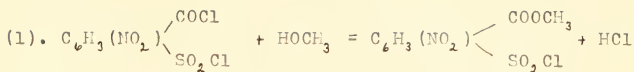
ACTION OF ALCOHOLS UPON THE UNSYMMETRICAL CHLORIDE OF
PARANITROORTHOSULPHOBENZOIC ACID.

The first one to study the action of alcohols upon the chlorides of paranitroorthosulphobenzoic acid was Kastle⁽¹⁾. He worked with the product of the reaction of phosphorus pentachloride upon the acid potassium salt of paranitroorthosulphobenzoic acid, a substance which he considered a chemical individual. We now know it to be a mixture of the symmetrical and unsymmetrical chlorides. Kastle found that the substance dissolved readily in methyl alcohol with the evolution of heat and upon cooling beautiful crystals were obtained.

This substance proved to be the paranitroorthosulphonchloride of methyl benzoate. However, if the alcoholic solution of the chloride was boiled for a time it became acid and this acid was shown to be the acid methyl ester of paranitroorthosulphobenzoic acid. The sulphonchloride was also changed to the acid ester by boiling with alcohol.

The following equations were given to explain these

(1) Loc. cit.



(1)

Henderson then studied the action of alcohols upon the symmetrical chloride. He found that, when that chloride was dissolved in methyl alcohol and then cooled, no sulphon-chloride came out. Any substance that did separate proved to be the unchanged chloride. ~~When~~ the alcoholic solution ~~was~~ ^{boiled} boiled for a time, the acid methyl ester described by Kastle was obtained. Ethyl alcohol acted in an ~~analogous~~ ^{analogous} way. He modified the conditions of the experiment in various ways, but failed entirely to get the sulphonchloride from the symmetrical chloride. A small quantity of the unsymmetrical chloride that he had in his possession did give, with ethyl alcohol, a substance melting at 68° and corresponding to the sulphonchloride described by Kastle.

It was thought best to study now the action of alco-

holds upon the symmetrical chloride to see if the results explained the formation of the sulphonchloride from the mixed chlorides.

I. ACTION OF METHYL ALCOHOL UPON THE UNSYMMETRICAL CHLORIDE.

a. Paranitroorthosulphonchloride of Methyl Benzoate.

$C_6H_3(NO_2) \begin{cases} COOCH_3 \\ SO_2Cl \end{cases}$ - A small portion of the chloride was added to a little methyl alcohol. It dissolved readily. Upon putting the solution on ice there was a rapid separation of crystals. These were filtered off and recrystallized from a little methyl alcohol. Small thick prisms were obtained melting at 82° .

b. Acid Methyl Ester of Paranitroorthosulphobenzoic

Acid $C_6H_3(NO_2) \begin{cases} COOCH_3 \\ SO_2OH \end{cases}$ - When the unsymmetrical chloride is boiled with alcohol for a short time an acid solution is obtained that does not become cloudy on the addition of water. The alcoholic solution evaporates to a syrup which finally solidifies to a crystalline mass. The following salts were made to identify this acid:

Sodium Methylparanitroorthosulphobenzoate,

$\text{C}_6\text{H}_3(\text{NO}_2) \begin{cases} \text{COOCH}_3 \\ \text{SO}_2\text{ONa} \end{cases}$ - This salt was obtained by carefully neutralizing the acid with a dilute solution of sodium carbonate. It crystallized from a concentrated solution in transparent plates.

0.1955 grams heated to 170° lost 0.0003 gram.

0.1952 gram gave 0.0488 gram Na_2SO_4

calculated for $\text{C}_6\text{H}_3(\text{NO}_2) \begin{cases} \text{COOCH}_3 \\ \text{SO}_2\text{ONa} \end{cases}$ Found,

Na 8.12 8.13

Potassium Methylparanitroorthosulphobenzoate,

$\text{C}_6\text{H}_3(\text{NO}_2) \begin{cases} \text{COOCH}_3 \\ \text{SO}_2\text{OK} \end{cases}$ - This salt was obtained by carefully neutralizing the acid with a dilute solution of potassium carbonate. It is fairly soluble in cold water from which it crystallizes in beautiful iridescent plates.

I. 0.1238 gram gave 0.0370 gram K_2SO_4 .

II. 0.1604 gram gave 0.0473 gram K_2SO_4

Calculated for Found,

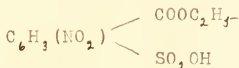
$\text{C}_6\text{H}_3(\text{NO}_2) \begin{cases} \text{COOCH}_3 \\ \text{SO}_2\text{OK} \end{cases}$ I. II.

13.18 13.39 13.21

2. ACTION OF ETHYL ALCOHOL UPON THE UNSYMMETRICAL CHLORIDE.

a. Paranitroorthosulphonchloride of Ethyl Benzoate

$$\text{C}_6\text{H}_3(\text{NO}_2) \begin{cases} \text{COOC}_2\text{H}_5 \\ \text{SO}_2\text{Cl} \end{cases}$$
 This substance was made by dissolving the unsymmetrical chloride in ethyl alcohol and cooling the solution. Beautiful white heavy needles separated at once. On recrystallization from ethyl ^{alcohol} they melt sharply at 68° .

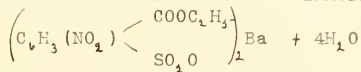
 b. Acid Ethyl Ester of Paranitroorthosulphobenzoic Acid


A few grams of the unsymmetrical chloride were dissolved in ethyl alcohol and boiled in a flask connected with a return condenser until a small portion dissolved in water to a clear solution. A very acid solution was thus obtained which evaporated to a syrup without crystallizing. On long standing, however, this syrup did solidify to a crystalline mass.

The acid is also obtained by dissolving the unsymmetrical chloride in more alcohol than is necessary to keep the above sulphonchloride in solution and allowing this solution to evaporate at the room temperature.

SALTS:

BARIUM ETHYLPARANITROORTHOSULPHOBENZOATE, -



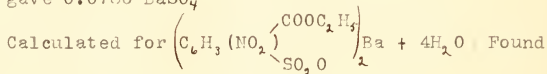
This salt was obtained by neutralizing the above acid solution with pure barium carbonate, heating nearly to boiling, filtering while hot and allowing to cool slowly.

The solution filled with long white needles. It was recrystallized several times to free it from any possible barium chloride that might be present.

The salt is very soluble in hot water, but slightly in cold.

0.2549 gram lost by heating to 170° , 0.0238 gram H_2O

0.2311 gram gave 0.0786 BaSO_4

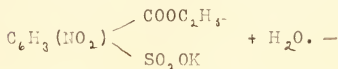


H_2O	9.51	9.34
----------------------	------	------

Calculated for the dried salt.

Ba	20.00	20.02
----	-------	-------

POTASSIUM ETHYLPARANITROORTHOSULPHOBENZOATE, -



This salt was made by neutralizing the free acid with a solution of potassium carbonate. It is very soluble

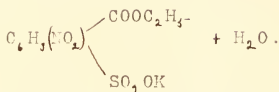
in water crystallizing from a concentrated solution in short heavy prisms.

0.2763 gram lost by heating to 170°C . 0.0150 gram H_2O

0.2458 gram of dried salt gave 0.0699 gram K_2SO_4

Calculated for

Found .



H_2O

5.42

5.43

Calculated for dry salt.

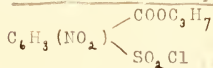
K

12.59

12.75

3. ACTION OF PROPYL ALCOHOL UPON THE UNSYMMETRICAL CHLORIDE

a. Paranitroorthosulphonchloride of Propyl Benzoate .



A portion of the symmetrical chloride was dissolved in warm propyl alcohol. Upon cooling large thin plates of the sulphorchloride separated. After recrystallization from warm propyl alcohol they melted at 76° .

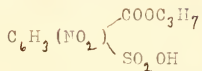
Analysis:

0.3273 gram gave 0.1523 gram AgCl .

0.2743 gram gave 0.1276 gram AgCl .

Calculated for $C_6H_3(NO_2) \begin{cases} COOC_3H_7 \\ SO_2Cl \end{cases}$		Found	
		I.	II.
Cl	11.51	11.50	11.51

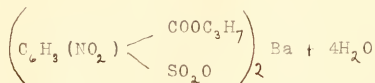
b. Acid Propyl Ester of Paranitroorthosulphobenzoic Acid



A few grams of the unsymmetrical chloride were boiled with propyl alcohol in a flask connected with a return condenser until a solution was obtained that did not turn cloudy with water. It was then evaporated to a syrup. This syrup dissolved easily in water to a clear very acid solution that decomposed carbonates easily.

SALTS:

BARIUM PROPYLPARANITROORTHOSULPHOBENZOATE -



This salt was obtained by neutralizing the acid solution obtained above with pure barium carbonate. It crystallizes well from warm water in long needles with a somewhat greenish hue. The crystals are easily soluble in warm water, less so in cold. They contain four molecules of wa-

ter of crystallization which is driven off below 170° .

0.2337 gram lost 0.0219 gram on heating to 170° .

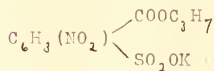
0.2118 gram of dried salt gave 0.0689 BaSO_4 .

Calculated for		Found
$\left(\text{C}_6\text{H}_3(\text{NO}_2) \begin{array}{l} \diagup \text{COOC}_3\text{H}_7 \\ \diagdown \text{SO}_2\text{O} \end{array} \right)_2 \text{Ba} + 4\text{H}_2\text{O}$		
H_2O	9.17	9.37

Calculated for dried salt.

Ba	19.26	19.15
----	-------	-------

POTASSIUM PROPYLPARANITROORTHOSULPHOBENZOATE



This salt was obtained in the usual way. It crystallized from a concentrated solution in small heavy needles. It is easily soluble in both hot and cold water.

0.1750 gram lost nothing on heating to 170° .

0.1750 gram gave 0.0471 gram K_2SO_4 .

Calculated for		Found
$\text{C}_6\text{H}_3(\text{NO}_2) \begin{array}{l} \diagup \text{COOC}_3\text{H}_7 \\ \diagdown \text{SO}_2\text{OK} \end{array}$		
	11.92	12.06

The results just described taken with those of Hen-

Henderson on the action of alcohols upon the symmetrical chloride explain more fully the results obtained by Kastle.

The sulphonchloride that he first obtained came from ^{phos} ~~his~~ unsymmetrical, ^{chloride} while the acid ester is seen to be the final product of the action of alcohols upon both chlorides. The acids obtained by Kastle from the mixed chlorides, those by Henderson from the symmetrical and those by the author from the unsymmetrical chloride appear to be identical.

PART III.

THE ACTION OF PHENOL IN AMMONIA SOLUTION UPON THE TWO
CHLORIDES OF PARANITROORTHOSULPHOBENZOIC ACID.

(1)

Remsen and McKee had obtained a substance which they called phenyl orthosulphamidobenzoate by heating the reaction mixture from the symmetrical chloride of orthosulphobenzoic acid and phenol with dilute ammonia. In an article by Stein and List on the chlorides of orthosulphobenzoic acid they state that they have been unable to obtain it either by treating the reaction mixture of chloride and phenol with ammonia or from the orthosulphonchloride of phenyl benzoate. They remark that according to their experiments the substance does not seem to be capable of existence. This led Humphreys to investigate the question with the result that while he was not able to get it from the orthosulphonchloride he could get it from the reaction of phenol, symmetrical chloride, and dilute ammonia.

(2)

As a further proof that such a body was formed it

As a further proof that such a body was formed it

(1) Loc. cit.

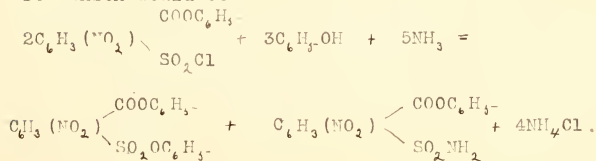
(2) Ber d. Chem. Ges. 31, 1648.

was thought best to repeat ^{the} ~~Humphreys's~~ ^{of Humphreys} work, using the chlorides of paranitroorthosulphobenzoic instead of those of orthosulphobenzoic acid.

The results ~~were entirely such as to~~ confirm the work of Remsen and McKee and of Humphreys.

Two grams of the symmetrical chloride were melted with an equal quantity of phenol and covered with dilute ammonia water. The oily mass hardened very slowly. After two days' standing the mass was well washed, then dissolved in hot alcohol. On cooling needle-shaped crystals separated that proved to be the diphenyl ester of paranitroorthosulphobenzoic acid. The alcoholic filtrate was allowed to evaporate at the room temperature and gave finally heavy prisms resembling the unchanged chloride but melting at 135° . Analysis proved them to be ~~those of~~ phenyl paranitroorthosulphamidobenzoate.

The course of the experiment was varied in many ways but the only result was the one given above, the equation for which would be



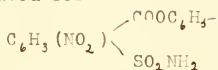
Analysis:

0.3221 gram gave 0.3754 CO_2 and 0.0993 gram H_2O

0.2366 gram gave 0.0204 gram N.

0.5172 gram gave 0.0445 gram N.

Calculated for



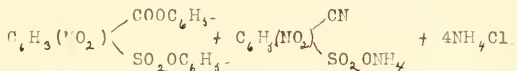
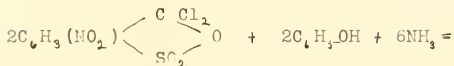
C	48.45	48.71	
H.	3.10	3.42	
N.	8.69	8.62	8.61

The action of phenol and ammonia was tried also upon the unsymmetrical chloride. Equal parts of the unsymmetrical chloride and phenol were melted together and treated with dilute ammonia.

The oily mass soon solidified. It was then washed and dissolved in alcohol. Crystals of the diphenyl ester separated as in the previous experiment but the alcoholic solution did not give any sulphonamide on evaporation. As (1) Gray has shown that the action of ammonia upon the unsymmetrical chloride is to form the ammonium salt of paranitrocyanbenzenesulphonic acid it is likely that some of

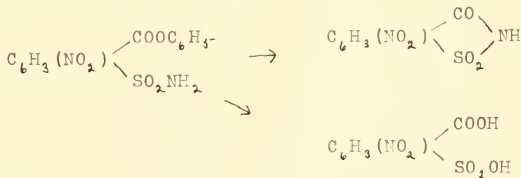
(1) Loc cit.

this substance was also formed in this experiment.



The action of caustic alkalies, ammonia, or water is strictly comparable to the action of the same reagents upon the orthosulphonamide of phenyl benzoate.

A weak solution of potassium hydroxide causes the formation of the potassium salt of the nitrobenzoic sulphinid. If the sulphonamide is heated a few moments with strong alkali, then acidulated characteristic crystals of the acid potassium salt of paranitroorthosulphobenzoic acid are observed:



The action of ammonia was very slow. If the boiling is kept up for five or more hours the reaction was complete and nitrobenzoic sulphinid was formed.

The action of water was more slow. This experiment

was kept up for five days without complete change taking place. There was some action, however, as the solution became gradually more bitter and gave more of a precipitate with bromine water. The common product of the action of weak alkalies, ammonia, and water upon the paranitroortho-sulphonamide of phenyl benzoate is nitrobenzoic sulphinide,

Conclusions.

This investigation has had the following results:

1. Three cases have been found in which compounds have been formed by the action of certain reagents upon one of the chlorides which we have not been able to form from the other chloride.

- a. Paranitroorthosulphonch chloride of phenyl benzoate was formed by the action of phenol on the unsymmetrical chloride but not at all from the symmetrical chloride. Ortho and para cresols act in a similar manner.

- b. Paranitroorthosulphonch chloride of ethyl benzoate was formed by the action of ethyl alcohol upon the unsymmetrical chloride. Methyl alcohol and propyl alcohol act in a similar manner.

c. Paranitroorthosulphonamide of phenyl benzoate was formed by the action of phenol and ammonia upon the symmetrical chloride but not at all from the unsymmetrical chloride.

2. The action of heat upon mixtures of symmetrical chloride and various phenols and upon mixtures of unsymmetrical chloride and the same phenols is outwardly the same in each case. Sometimes the unsymmetrical seems to act a little more readily. The resulting ethereal salts formed are of two classes. The symmetrical chloride gives ethereal salts of the class $C_6H_3(NO_2) \begin{cases} COOR \\ SO_2OR \end{cases}$ while salts of the class $C_6H_3(NO_2) \begin{cases} COOR \\ SO_2Cl \end{cases}$ are formed entirely from the unsymmetrical chloride.

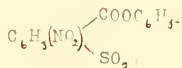
3. The action of phenol upon either chloride in alkaline solution was the formation of the diesters as the end product. By this method di-~~acetyl~~-esters were formed from phenol, ortho and para cresols, ortho, meta and para nitrophenols and B-naphthol. By modifying the conditions of the experiments ester chlorides were formed from phenol and ortho cresol.

4. The action of methyl, ethyl and propyl alcohols upon the unsymmetrical chloride was the formation first of the corresponding sulphonchlorides $C_6H_3(NO_2) \begin{cases} COOR \\ SO_2Cl \end{cases}$ then

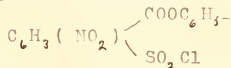
these bodies passed to the corresponding acids

$$\text{C}_6\text{H}_3(\text{NO}_2) \begin{cases} \text{COOR} \\ \text{SO}_2\text{OH} \end{cases}$$
 by the action of heat. The salts of these acids were the same as the salts of the acids made by the action of these alcohols upon the symmetrical chloride.

5. The action of reagents upon paranitroorthosulphon-chloride of phenyl benzoate were such as to indicate the presence of the group



in that body. This gives the structure



for the substance in question.

Biographical.

The author of this dissertation was born in Rochester, New York, on the 18th of November, 1869. His early education was received in the public schools of that city. After leaving the public schools he was engaged in the drug business for a number of years, leaving that to enter the University of Rochester in 1891. He there pursued the scientific course, taking the degree of Bachelor of Science in 1895. The three years following he was science teacher in the public high school at Geneva, New York. Entering the Johns Hopkins University in the fall of 1898, he has since been engaged upon graduate work with Chemistry as his principal subject, Physical Chemistry his first subordinate and Botany his second subordinate subject. Since the fall of 1899 he has acted as assistant to Dr. Gilpin in the laboratory work of the course in minor Chemistry.

